Electrochemical Deposition of Novel Semiconductors for Thermoelectric Devices

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Electrochemical deposition (ECD) is a promising alternative approach to bulk synthesis of materials for fabrication of thermoelectric microdevices [1]. A thermoelectric device consists of several pairs of p- and n-type elements connected electrically in series and thermally in parallel. Each device can be fabricated to function as a power generator, cooler or heater; therefore, thermoelectric microdevices are of interest for a variety of space and terrestrial applications [2].

There is a great need for miniaturization of thermoelectric devices. Shrinking the size of the thermoelements, or legs, makes it possible to handle significantly higher heat fluxes, as well as to operate at much lower currents and higher voltages, which are more compatible with electronic components [3]. State-of-the-art fabrication and processing of semiconducting materials for thermoelectric elements have reached mechanical limits [4]. The limit on the height of legs made from bulk material is 100 to 200 μm minimum; this limit is imposed by mechanical considerations. The maximum number of legs on a single device, 100 to 200 maximum, is limited by mechanical and manufacturing considerations. By electrochemically depositing thermoelectric materials through photoresist patterns on metallized silicon substrates, we have produced devices with tens of thousands of micrometer-sized legs (20 to 60 μm high) [4,5].

Another advantage of ECD is that it is simple, fast and inexpensive. Typical growth rates are 4 to 15 μm/hour. Experiments were usually run at room temperature in a three-electrode configuration (Pt counter electrode, Pt or Au working electrode and a SCE reference). The standard electrolytes contained on the order of 10^{-3} M concentrations of oxidized high purity elements, salts and/or chelating agents in aqueous 1 M HNO_3 (pH = 0). The experimental parameters varied in this study included deposition potential, temperature, metal concentrations, solution pH, stirring rate, Ar de-aeration and substrate quality. Film thickness, surface morphology, atomic composition, crystallographic orientation and the Seebeck coefficient were measured to determine the quality of the electrochemically deposited legs for device applications.

Electrochemical techniques have been developed for the growth of n-type Bi_2Te_3 and $Bi_2Te_{3-x}Se_x$ and p-type $Bi_{2-x}Sb_xTe_3$ compositions, and have been previously reported [2,5]. The materials are oriented, and have Seebeck coefficients of up to -180 μV/K for n-type and +200 μV/K for p-type materials. These compounds are optimal for thermoelectric applications near room temperature, 200 to 500 K. Our recent efforts have focused on the development of novel thermoelectric materials, such as Zn_4Sb_3 and $CoSb_3$-based skutterudites, which function best at elevated temperatures (400 to 800 K) and are now under study at JPL in bulk form [6]. The ultimate interest lies in using both high and low temperature materials to make segmented thermoelectric legs for a device designed to operate from 200 to 800 K. We have also recently deposited PbTe in both the p- and n-type forms [5], which led to studies of layered compounds, based on both Bi_2Te_3 and PbTe, such as $PbBi_4Te_7$ and $Pb_4Bi_2Te_7$. This paper reports progress in developing ECD methods for obtaining these novel thermoelectric materials and structures, as well as optimizing their morphology and transport properties for thermoelectric microdevices.

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